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CHEMICAL SAMPLING DOWNSTREAM OF LEAN, FLAT HYDROGEN AND PROPANE FLAMES

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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E-523

CK-1

SUMMARY

Decay profiles were obtained for carbon monoxide and for hydrogen downstream of lean, flat propane-air, propane-oxygen-argon, hydrogen-air, and hydrogen-oxygen-argon flames. Both carbon monoxide and hydrogen were present in large excess of equilibrium amounts. Sampling was done by uncooled quartz orifice probes and analysis by gas chromatography. Consideration of effects of diffusion and of chemical reactions within the probe showed that decay profiles could be converted to time rates of decay in the burned gas. However, because of the complicated shape of the decay profiles, results could be considered only qualitative. For both carbon monoxide and hydrogen, the decay rate increased with pressure, temperature, and oxygen concentration. For both hydrogen and carbon monoxide, lower decay rates were found with argon as a diluent than with nitrogen.

The fact that the hydrogen decay rate downstream of hydrogen-air flames was larger than that downstream of propane flames suggested that the primary decay reaction in both cases involved hydrogen and that the decay of carbon monoxide occurred through the water-gas equilibrium. Some evidence was found, however, for contending that the primary decay process downstream of propane flames involved carbon monoxide instead.

INTRODUCTION

Within the last few years, several independent groups of studies have been reported which involve the sampling of the zone immediately downstream of burner flames. The fact that quantities of combustion intermediates were found in large excess of equilibrium amounts suggested that composition profiles for the decay of these intermediates to equilibrium concentrations could be interpreted so as to yield reaction rates for chemical processes at flame temperatures (refs. 1 to 4). In these studies, probing was done by actual sample withdrawal through quartz orifice probes. In the work of references 1 to 3 the burned gas samples were analyzed primarily for carbon monoxide; however, in that of reference 4 complete analyses were obtained of the burned gases from rich hydrogen-oxygen-carbon-dioxide flames.

In the work of references 1 and 2, attempts were made to obtain decay profiles for hydrogen downstream of lean hydrocarbon-air flames analogous to those obtained for carbon monoxide; these attempts were not successful. It has recently been pointed out that such profiles, even if they could be obtained, might be rather difficult to interpret without additional information (ref. 5). This is because the concentration of OH in the burned gas would be expected to greatly exceed the concentration of H_2. Thus, the analysis of a quenched sample might show large quantities of H_2 produced mainly by the recombination of OH in the probe to give H_2 and O_2. Such a recombination mechanism has been proposed in reference 6 as one alternative explanation of the stable products formed from the quenching of a water vapor discharge.

E-523

In the present study decay profiles have actually been obtained for hydrogen downstream of lean hydrogen-oxygen and propane-oxygen flames with nitrogen and argon as diluents. The effects of pressure, flame temperature, and oxygen concentration were examined. It was hoped that the behavior of such profiles over a wide range of experimental conditions would give some information regarding the extent to which the profiles themselves represented the decay of hydrogen in the burned gas.

As a check on the reliability of the sampling method, several profiles were obtained for carbon monoxide decay downstream of propane flames under experimental conditions approximating those of reference 2. The effect of pressure on carbon monoxide decay was then examined, and results for carbon monoxide were compared with those for hydrogen.

As in references 1 to 4, samples were withdrawn through uncooled quartz orifice probes. Chemical analysis was done by gas chromatography, which gave particularly sensitive and reproducible results for hydrogen. Flames were stabilized on cooled porous burners; this allowed a direct comparison with results of reference 2.

SYMBOLS

$\mathcal{D}$ diffusion coefficient, cm^2/sec

P pressure, cm Hg

T temperature of downstream zone, $^{\circ}K$

t time, sec

v velocity of burned gas, cm/sec

X distance from burner, cm

x mole fraction

EXPERIMENTAL PROCEDURE

The hydrogen, argon, and oxygen used were obtained in tanks from stock. The propane used was of a chemically pure grade. Laboratory service air was used as combustion air. All materials were used without further purification. The various constituents of the initial mixture were metered separately through calibrated critical-flow orifices and then mixed in flow.

Measurements were made above two burners of similar design but different size. The smaller burner had a circular plate of sintered copper shot 2 inches in diameter and 1/4 inch thick which was sintered to a copper jacket. A cooling coil of 3/16-inch-outside-diameter copper tubing was likewise sintered into the base of the plate. A sketch of this burner is shown in figure 1. The top surface of the burner plate was machined and then etched with dilute nitric acid to obtain maximum smoothness. The other burner had a sintered plate 4 inches in diameter and 5/16 inch thick. On both burners the flames produced were smooth and flat in appearance and hot-wire anemometer traverses showed no large velocity irregularity in cold flow. With such a burner, the temperature of the flame could be controlled by controlling the stream velocity ahead of the burning mixture (ref. 7).

CK-1 back

Determination of Temperature and Pressure

Wherever possible, equivalence ratios and burning velocities were chosen so that temperatures determined in the work of reference 8 by measurement with coated thermocouples could be applied. On both burners, these temperatures were checked by measuring the quantity of heat abstracted from the flame by water flowing through the cooling coil. An equilibrium flame temperature could then be calculated based on the quantity of heat removed. It was assumed that this temperature could be taken to represent the temperature of the burned gas immediately downstream of the flame. The two sets of temperatures were generally in reasonable agreement, seldom differing by more than about 40° K. The few cases where a large discrepancy was found are discussed in a later section. No flame temperatures are reported for propane-oxygen-argon flames in reference 8. Therefore only temperatures based on heat abstraction could be obtained for such flames.

The burners were set in the base of a low-pressure combustion chamber connected to a plenum chamber and vacuum pump. The pressure in the combustion chamber was controlled by balancing the pumping with a variable air bleed. It could be controlled to ± 3 millimeters of mercury and, once set, showed no tendency to drift or fluctuate.

Sampling and Analysis

Gas samples were withdrawn through uncooled quartz probes of 3-millimeter inside diameter; these were drawn down, as sharply as possible, to an orifice tip about 25 microns in diameter. The orifice size was adjusted, with change in chamber pressure, to provide a roughly constant sampling rate. For a particular flame at constant pressure, a moderate change in orifice size or shape did not change the slope of the decay profile. Occasionally, however, on making duplicate runs, some change occurred in the level of carbon monoxide or hydrogen found. An effect of this kind is reported in reference 2. It is possible that this difference can be attributed to a systematic error of a few tenths of a millimeter in recording the position of the probe relative to the burner.

As shown in figure 1, the probe was connected to a brass tube which was led out the bottom of the combustion chamber. A flexible connection led from the base of the tube to a vacuum line where gas samples were collected. The tube was supported on an outer hollow shaft whose height could be adjusted by a micrometer screw. By this arrangement, the probe was free to move through an arc; thus, its position relative to the center of the burner could not be rigidly fixed. However, during the course of a profile determination, the probe was held approximately over the center as the height above the burner plate was changed. The height of the probe tip was measured with reference to the burner rim by a cathetometer which could be read to 0.05 millimeter. Because of parallax, irregularities in the probe tip, and the obscuring effect of radiation from the probe tip, the position of the orifice may have been uncertain to ±0.2 millimeter. No samples were withdrawn from the luminous portion of the flame, and, in interpreting results, no attempt was made to account for the change in the height of the flame above the burner plate with change in burning velocity, pressure, and equivalence ratio.

The gas samples were collected in 300-milliliter sampling bottles which were immediately pressurized to 1 atmosphere for analysis. The final pressure in the sampling line was always less than 1/10 the pressure in the combustion chamber so that critical flow across the probe orifice was maintained. Analyses were performed on a Perkin-Elmer Vapor Fractomer, model 154B.

Separation columns and carrier gases were chosen with regard for the particular components sought. For carbon monoxide determination, helium was the carrier; for hydrogen determination argon was used as the carrier. Thus, for propane-air and hydrogen-air flames, samples were analyzed for oxygen and nitrogen, in addition to carbon monoxide or hydrogen. Since no analyses were obtained for water or carbon dioxide, concentrations in the burned gas were expressed relative to the concentration of nitrogen. To a fair approximation, the mole fraction of

E-523

nitrogen is the same in the burned and unburned gases. Thus, the measurement of $[CO]/[N_2]$ or $[H_2]/[N_2]$ allows estimation of $[CO]/[C_3H_8]$ or $[H_2]/[C_3H_8]$ across the flame.

In analyzing for hydrogen downstream of flames with argon as the diluent, no argon peak was obtained; therefore concentrations could not be expressed relative to argon. However, a rough estimate of the composition could be obtained based on the oxygen peak. The use of nitrogen as the carrier would have given an argon peak; however, with the nitrogen carrier, separation of oxygen and argon could not be obtained.

In some cases relative concentrations were found by direct measurement of peak areas. Area ratios obtained were converted to concentration ratios by factors, obtained experimentally, relating concentrations and peak areas. If peaks were reasonably sharp, however, greater accuracy was obtained with a great saving of time by comparing peak heights with those for known mixtures.

TREATMENT OF DATA

The treatment of results rested on the assumption that decay profiles represented the decay of carbon monoxide and hydrogen in the burned gas through the effects of chemical reaction and of diffusion in the downstream direction. It was found in references 1 to 3 that $d \log [CO]/dX$, where X is distance downstream, was constant for a single flame; the fact that it was constant showed that the rate of disappearance of carbon monoxide through chemical reaction was first-order with respect to carbon monoxide. For purposes of comparison, the data presented here are plotted as $\log [CO]$ or $\log [H_2]$ against distance. If the total flux of carbon monoxide or hydrogen can be expressed as the sum of fluxes due to chemical reaction and diffusion in the direction of flow, then the equation of reference 3 applies

$$\frac{d \ln [\ ]}{dt} = - \frac{d \ln [\ ]}{dX}\left(v - \frac{d \ln [\ ]}{dX}\right) \mathscr{D} \tag{1}$$

where $[\ ]$ represents the concentration of any species in the burned gas. The value of the diffusion coefficient $\mathscr{D}$ in equation (1) was calculated as the diffusion coefficient of the species in brackets into nitrogen at flame temperature and was assumed to vary as $T^{5/3}$. It is seen from equation (1) that, in any region where v and $\mathscr{D}$ are constant, the fact that $d \log [\ ]/dX$ is constant is sufficient to imply that the reaction is first-order with respect to the species in the brackets.

E-523

RESULTS AND DISCUSSION

General Considerations

Experimental results are summarized in table I for the 2- and 4-inch burners. Entries include description of the unburned mixture, flame temperature, chamber pressure, and all pertinent results obtained from analysis of samples. Most of the decay profiles obtained are shown in the figures. From inspection of the table and figures, several general features of the results can be seen. These are discussed in the following sections.

Oxygen concentration in the burned gas. - Measured values of x_{O_2}/x_{N_2} in the burned gas are in satisfactory agreement with approximate calculated values based on the composition of the initial mixture. Calculated values can only be approximate for several reasons. First, essentially nothing is known beforehand regarding concentrations of stable and unstable intermediates in the burned gas except that they are probably all in excess of equilibrium. Consequently, even if the concentrations of stable intermediates such as carbon monoxide and hydrogen are known, the burned gas composition is not sufficiently well defined to give an accurate value for x_{O_2}/x_{N_2}. Second, even if specifying the concentration of carbon monoxide and hydrogen in the burned gas did give an adequate representation of its composition, the existence of fairly sharp decay profiles for these species means that the oxygen concentration in the burned gas also changes with distance downstream. Thus, for the propane-air flames discussed in this report, the values of x_{O_2}/x_{N_2}, based on measured values of carbon monoxide and hydrogen concentrations, can vary by about 10 percent with distance, so that single values listed in the table only represent fairly rough average values. The hydrogen flames studied were considerably leaner, giving a much larger excess of oxygen in the burned gas. For such flames the relative spread would be much less.

The fact that the carbon monoxide and hydrogen concentrations decrease with increasing downstream distance implies a corresponding decrease in oxygen concentration and a profile which should be readily detectable, at least for the propane-air flames studied. In practice, such profiles were not generally found. This could have represented the influence of small undetected air leaks or the fact that the oxygen concentration in the burned gas varied slightly across the downstream zone either because of inward diffusion of oxygen or slight irregularities in the flame.

In working with the 2-inch burner, it was found that, as pressure, burning velocity, and calculated values of x_{O_2}/x_{N_2} in the burned gas

E-523

were decreased below certain critical limits, the observed values of x_{O_2}/x_{N_2} increased far beyond calculated values. In particular, for propane-air flames at an initial equivalence ratio greater than 0.80 and burning velocities of about 15 to 20 centimeters per second, no satisfactory profiles could be obtained below atmospheric pressure, whereas for hydrogen-air flames at an initial equivalence ratio of 0.75 and a burning velocity of 30 centimeters per second, satisfactory concentrations of oxygen in the burned gas were found at pressures as low as 1/4 atmosphere. However, for burning velocities near 13 centimeters per second decay profiles for hydrogen-air flames at an equivalence ratio of 0.75 at a pressure of 31 centimeters of mercury showed a large excess of oxygen in the burned gas. With the 4-inch burner, however, the range of conditions giving satisfactory observed values of x_{O_2}/x_{H_2} was greatly extended. Such behavior strongly suggested that under favorable circumstances secondary air was diffusing into the downstream zone in a direction perpendicular to the direction of flow. The fact that the atmosphere around the burner was not controlled made it reasonable to assume that the gas diffusing in had approximately the composition of air.

Since the region of analysis is well within the potential core of the jet, such diffusion would be wholly unexpected. However, several observations tended to confirm that it was taking place. First, when a low stream of helium was directed below and away from the flame, analysis of the burned gas at a point a few millimeters above the center of the flame showed that about 3 percent helium was present.

Second, analysis downstream of flames in which argon was used as the diluent always showed from 2 to 6 percent nitrogen present in the burned gas, depending on the initial conditions. Even within a single profile, the concentration of nitrogen found was not constant, but fluctuated. This behavior suggested, of course, that air was leaking into the sample during either sampling or analysis, in spite of precautions taken. As an experimental check on the effect of such leakage, oxygen was run through the burner immediately before and following a profile determination; the effluent gas was analyzed for nitrogen. With the 4-inch burner, the concentration of nitrogen found varied from about 1 to 3 percent. The fact that some nitrogen was found means that some leakage might have occurred. However, the amount of nitrogen found downstream of a flame was always greater than amounts found in appropriate blank runs. These are certain indications that some inward diffusion was taking place, driven by the temperature and density gradients produced by the flame and, perhaps, by the velocity gradient caused by the jet itself.

Since any appreciable diffusion of secondary air would cause lowering of the temperature of the downstream zone, runs for which much diffusion was found to have occurred were not considered further.

General appearance of decay profiles. - It can be seen from inspection of the figures that, in general, the decay profiles are not linear. If one chooses, they may be conveniently thought of as consisting of two parts. The part farther out from the flame is less steep and reasonably representable by a straight line on a semilogarithmic plot. In reference 2, all sampling was apparently done in this second region. The part closer to the flame zone is much steeper and shows definite curvature. If the length of the curved part increases with decreasing pressure, as do many distances associated with flames, it is quite conceivable that the data of references 1 and 3, which were obtained at very low pressures in the neighborhood of 4 centimeters of mercury, represent the inner, steep portion of the decay profile and are not, therefore, comparable with profiles reported for the outer portion at much higher pressures.

E-523

The fact that decay profiles show curvature when plotted semilogarithmically against distance downstream is noted in reference 5 on the basis of optical probing. The fact that similar curvature has been found from sample withdrawal measurements is some indication that there is a degree of equivalence between the two methods of probing. On the other hand, it is apparent that if semilogarithmic decay profiles are assumed to have constant slopes, such slopes will be, at best, indirectly related to the kinetics of reactions taking place in the burned gas. For purposes of comparison with data of reference 2 and to provide some basis for correlating present data, it will be assumed that the less steep portion of the profile is linear and that its slope can be used in equation (1) to obtain a decay rate.

Results for Propane-Air Flames

Results for carbon monoxide decay at atmospheric pressure. - Results at atmospheric pressure are summarized in entries 1 to 3 and 14 and 15 of table I. Comparison of entries 14 and 15 shows the general reproducibility of decay slopes for a given burner. Comparison of entries 1 to 3 with 14 and 15 shows the apparent effect of burner diameter. By interpolating results with respect to flame temperature and correcting for the small difference in oxygen concentration on the basis that the decay rate is proportional to the oxygen concentration at constant flame temperature (ref. 2), it is seen that the apparent change in decay rate is about 10 percent, which is not significant. Two decay curves, those corresponding to entries 1 and 2, are shown in figure 2. The data for entry 3 showed considerable scatter and the curve overlapped the curve for entry 2. Consequently, it is not shown in the figure.

The decay rates presently obtained compare well with those reported in reference 2, as does the increase with flame temperature. Also, at constant pressure, the rate increases significantly with oxygen concentration in the burned gas (entries 18 and 19); that is also reported in reference 2.

Results for carbon monoxide decay at reduced pressure. - Figure 3 shows decay profiles for carbon monoxide at four pressures between 1 atmosphere and 19 centimeters of mercury obtained on the 4-inch burner. As pressure was reduced, the burning velocity was held constant. It was assumed that, if burning velocity were held constant, flame temperature would not change significantly with change in pressure. It was found experimentally that the quantity of heat removed per mole of mixture did not change with change in pressure; flame temperatures calculated on this basis changed by only about 2° K for a tenfold change in pressure. However, results presented in table I of reference 9, based on thermocouple measurements, would seem to indicate that flame temperature does change with pressure at constant burning velocity, at least for lean hydrogen-air flames, and that the magnitude of the change depends on equivalence ratio. Thus for equivalence ratios above about 0.75 the change may be within the error of measurement. At lower equivalence ratios the change amounts to about 100° K for a change in pressure by a factor of 2. Although most of the measurements presently reported with change in pressure involve equivalence ratios of 0.75 or greater, there is the possibility of an experimental contradiction between present results and those of reference 9. This possibility should be borne in mind in evaluating the significance of the observed pressure dependence.

E-523

CK-2

The results, given in table I(b), show that the slope of the decay profile decreases with decreasing pressure. A cross plot of the decay rate against pressure, given in figure 4, shows that the rate increases with about the square root of the pressure, provided that the temperature remains nearly constant. If one applies the findings of reference 9 to propane-air flames, one might expect a change of at most 40° K over the pressure range shown in figure 6. This would have the effect of reducing the slope by about 15 percent.

Results for hydrogen decay downstream of propane-air flames. - Quantities of hydrogen in large excess of equilibrium were found downstream of lean propane-air flames. The concentration decayed so as to yield reasonably smooth profiles qualitatively similar to those obtained for carbon monoxide. Comparison of entries 4, 5, and 20 shows, once again, that there is no significant effect of burner diameter on the decay rate.

The effect of reduced pressure is shown in figure 5, and a cross plot of the decay rate against pressure is given in figure 4. It is seen that the change in the decay rate with pressure is similar to that found for carbon monoxide, increasing as the pressure to an exponent somewhat less than 1/2. Once again, one would expect that the change in flame temperature at constant burning velocity over the pressure range covered would be sufficiently small that correction of decay rates to constant temperature would not significantly change the pressure slope.

The effect of temperature on the slopes of decay profiles is given in entries 4 to 6 of table I and in figure 6. The number of data points is few and the uncertainty in the rate is certainly no less than ±10 percent. Nevertheless, it appears that the hydrogen decay rate increases with temperature to about the same extent as that for carbon monoxide. The effect of oxygen concentration in the burned gas, given in entries 6 and 7, is also similar to that found for carbon monoxide decay.

In figure 6 it is seen that the curve for 1915° K lies generally above that for 1790° K. However, at about 2 millimeters from the burner plate, the two curves cross, so that at small distances downstream the apparent level of hydrogen concentration is lower at the higher temperature. The simplest explanation for this behavior would be that, somewhere near 1900° K, the efficiency of the probe for quenching the hydrogen oxidation fails somewhat. As mentioned previously, a similar effect was found for carbon monoxide. It is possible, however, that the apparent crossing represents a consistent analytical error in one of the decay curves.

The generally reasonable sampling results for hydrogen suggest that recombination of OH in the probe occurs, in an overall fashion, as

$$4OH \rightarrow 2H_2O + O_2$$

so that the concentration of hydrogen in the burned gas is not directly affected by reactions occurring in the probe.

<u>Concentrations of carbon monoxide and hydrogen in the burned gas.</u> - Calculation of equilibrium concentrations in the burned gas, by the method of reference 10, indicates that the ratio $[CO]/[H_2]$ in the burned gas should increase with temperature from about 2.6 at 1730° K to 3.4 at 1970° K and be virtually independent of pressure. In the cases where $[CO]/[H_2]$ in the burned gas could be directly or nearly directly measured, the values ranged from 2.5 to 3.9 generally, though not consistently, increasing with temperature and pressure. Although the slopes of the carbon monoxide and hydrogen profiles are not too different, they are not identical either, so that $[CO]/[H_2]$ varies slightly with distance. Variation within a single run can be attributed to the effects of diffusion. The variation of the ratio among several runs can be attributed either to systematic progressive failure of the probe to quench the reaction of hydrogen relative to that of carbon monoxide with increasing pressure or to the observed random occasional inability to reproduce levels of concentration among several runs. The results tend to suggest, however, that the analysis of samples withdrawn from the flame does give, at least roughly, the composition in the burned gas, but that either the decay profiles are slightly affected by probe reactions or that equilibrium between carbon monoxide and hydrogen (i.e., a constant value of $[CO]/[H_2]$ in the burned gas at constant temperature and pressure) is not exactly maintained.

E-523

CK-2 back

Results for Propane-Oxygen-Argon Flames

Experimental results for the decay of hydrogen downstream of lean propane-oxygen-argon flames are shown in entries 10 to 13 and 23 to 25 of table I. Two decay profiles are shown in figure 7. A single decay profile for carbon monoxide is shown in figure 8 and the decay rate is given in entry 13(a). Comparison of entries 10 and 23 shows, once again, that there is no significant effect of burner diameter on the slope of the decay profile. It appears, however, that the use of argon as the diluent depresses the decay rate, at constant temperature, pressure, and oxygen concentration, by about a factor of 2 for both hydrogen and carbon monoxide. Since argon is known to be less efficient than nitrogen as a third body in recombination reactions (ref. 11), these results give some indication that the decay involves recombination.

The effect of flame temperature is small; in general, the decay rate increases with flame temperature in agreement with results for propane-air flames.

If one considers qualitatively the combined effects of temperature, pressure, oxygen concentration, and diluent on the decay rate, it seems reasonable to suggest that the primary reaction leading to the decay of hydrogen and carbon monoxide occurs either between molecular hydrogen and oxygen atoms or carbon monoxide and oxygen atoms. The increase in rates with increasing oxygen concentration would be explained by assuming a steady state between molecular oxygen and oxygen atoms. Since molecular oxygen is usually in large excess, the concentration of atoms would not vary much with distance at constant temperature. The increase in rate with temperature would occur, then, because the degree of dissociation of oxygen increases with temperature. The decrease in decay rate with decreasing pressure is smaller in magnitude than would be expected for a reaction involving triple collisions. However, this could come about because a decrease in oxygen atom concentration with decreasing density would be opposed by an increase in concentration due to an increase in dissociation.

More quantitative consideration, however, shows several discrepancies. In the first place, the decay rates appear to increase with the oxygen concentration to a power equal to or somewhat greater than 1. Recombination based on equilibrium between molecular oxygen and oxygen atoms would lead to an increase with the square root of the oxygen concentration. Second, the increase with temperature is much less than the calculated increase in oxygen atom concentration with temperature. This cannot be wholly accounted for from consideration of the fact that the amount by which the oxygen atom concentration exceeds equilibrium decreases somewhat with increasing temperature. Finally, even considering the effect of pressure on the degree of dissociation, the pressure effect on the decay rate is still too small. Thus, while the effect of a diluent suggests a recombination reaction, present results from propane-air flames do not give much further information on what reactions are involved.

Reference 5 proposes that carbon monoxide decay from lean propane-air flames occurs by recombination with oxygen atoms. Present results obtained downstream of propane-air flames are not wholly inconsistent with the proposal. However, these results could be equally well explained on the basis that the primary reaction involves hydrogen rather than carbon monoxide. In that case, one would expect the hydrogen decay rate in the absence of carbon monoxide to be larger than in burned gas containing carbon monoxide. A few measurements of that kind are described in the next section.

Results for Hydrogen Flames

A few decay profiles are shown (figs. 9 and 10) for the decay of hydrogen downstream of lean hydrogen-air and hydrogen-oxygen-argon flames with change in flame temperature. The concentration of hydrogen found increases with flame temperature, which indicates at least partial quenching efficiency on the part of the probe. The decay rates (table I(a)) increase with temperature in a fashion similar to hydrogen decay rates downstream of propane flames.

The flame temperatures calculated for hydrogen-oxygen-argon flames from heat abstraction were about 120° K lower than those obtained from the data of reference 8 at 1 atmosphere. However, the decay profiles were obtained at reduced pressure and at a low equivalence ratio, within the range of equivalence ratios at which the temperatures measured in reference 9 with thermocouples showed a decrease with decreasing pressure.

A series of data had been obtained for hydrogen-air flames which showed that between pressures of 1 and 0.25 atmosphere the decay rate was roughly proportional to the pressure at constant oxygen mole fraction and proportional to oxygen concentration at constant pressure. These data involved only the inner, steep portion of the profile, so that the calculated decay rates are not comparable with other data presented here. The sign and order of magnitude of the pressure and oxygen dependence are probably correct, however. Having some idea of these effects, one can compare decay rates for hydrogen obtained downstream of hydrogen and propane flames. It seems fairly certain that apparent decay rates downstream of hydrogen-air flames are significantly larger than for propane flames. This suggests rather strongly that the primary process downstream of propane flames involves hydrogen rather than carbon monoxide. The presence of carbon monoxide in the burned gas would serve to replenish the hydrogen, through the water-gas equilibrium, and thus decrease the apparent hydrogen decay rate. If this were the case, one would expect

E-523

the decay rate downstream of hydrogen-air flames to exceed the decay rate downstream of hydrocarbon flames by a factor of $\frac{[CO] + [H_2]}{[H_2]}$ (all concentrations being those found downstream of a hydrocarbon flame), that is, by a factor of about 4. Comparison of entries 9, 16, and 17 shows that this is approximately true.

It should be noted, however, that substitution of argon as a diluent for nitrogen appears not to have an effect on the decay rate, in contrast with the behavior for propane flames. Because of the leanness of the initial mixture and the consequent uncertainty of the flame temperature, an accurate comparison is not possible. In the event that the effect should be real, it could serve as evidence that the primary reaction downstream of hydrocarbon flames does involve carbon monoxide rather than hydrogen and that the mechanism of hydrogen decay is different downstream of hydrogen and hydrocarbon flames.

SUMMARY OF RESULTS

Chemical sampling studies downstream of lean propane and hydrogen flames yielded the following results:

1. For both carbon monoxide and hydrogen, plots of log concentration against distance from the burner plate were not generally linear. Such plots usually showed a steep curved region close to the flame and a flatter linear portion farther downstream.

2. On the assumption that the linear portions of the decay profiles were related to the decay rate, the following behavior was observed for carbon monoxide and hydrogen downstream of lean propane flames.

(a) The decay rate increased with flame temperature.

(b) The decay rate increased approximately as the square root of the pressure.

(c) The decay rate was roughly proportional to oxygen concentration in the burned gas.

(d) The relative concentrations of carbon monoxide and hydrogen found indicate that the water-gas equilibrium was maintained.

3. Results generally suggested that the primary decay reaction downstream of propane flames was a recombination reaction involving hydrogen. Some evidence was found, however, which indicated that the primary reaction involved carbon monoxide instead.

Lewis Research Center
National Aeronautics and Space Administration
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E-523

TABLE I. - SUMMARY OF DATA

Entry number	Fuel	Species	Diluent	Equivalence ratio	Burning velocity, cm/sec	Temperature, T, °K (based on measurements of ref. 8)	Pressure, P, cm Hg	$\frac{x_{O_2}}{x_{N_2}}$, (calculated)	Semi-log slope, cm^{-1}	Decay rate, sec^{-1}
(a) 2-Inch burner										
1	C_3H_8	CO	N_2	0.835	16.0	1855	74	0.045	2.69	304
2					20.2	1915	74	0.045	2.65	376
3					25.0	1970	74	0.045	2.30	405
4		H_2	N_2	0.835	25.0	1970	74	0.045	1.54	296
5					20.2	1915	74	0.045	1.84	299
6					12.0	1790	74	0.045	1.98	206
7				0.70	12.3	1725	74	0.08	4.01	600
8	H_2	H_2	N_2	0.70	30.0	1670	31	0.08	2.41	575
9					56.0	1850	31	0.08	1.88	800
10	C_3H_8	H_2	A	0.835	10.0	[a]1805	74	0.045	1.57	143
11					14.0	[a]1870	74	0.045	1.31	150
11a					20.0	[a]2080	74	0.045	1.27	216
12	H_2	H_2	A	0.600	20.0	1670	31	0.11	3.74	877
13					30.0	1785	31	0.11	3.71	1050
13a	C_3H_8	CO	A	0.835	14.0	[a]1870	74	0.045	1.89	181
(b) 4-Inch burner										
14	C_3H_8	CO	N_2	0.865	16.0	1870	74	0.04	2.37	262
15									2.10	230
16							38	0.04	1.25	139
17							27	0.04	1.18	136
18							19	0.04	0.95	112
19				0.800	17.1	1830	19	0.06	1.55	212
20		H_2	N_2	0.865	16.0	1870	74	0.04	2.08	280
21							45	0.04	1.79	264
22							27	0.04	1.17	180
23			A	0.835	10.0	[a]1805	74	0.045	1.46	133

[a]Based on heat abstraction.

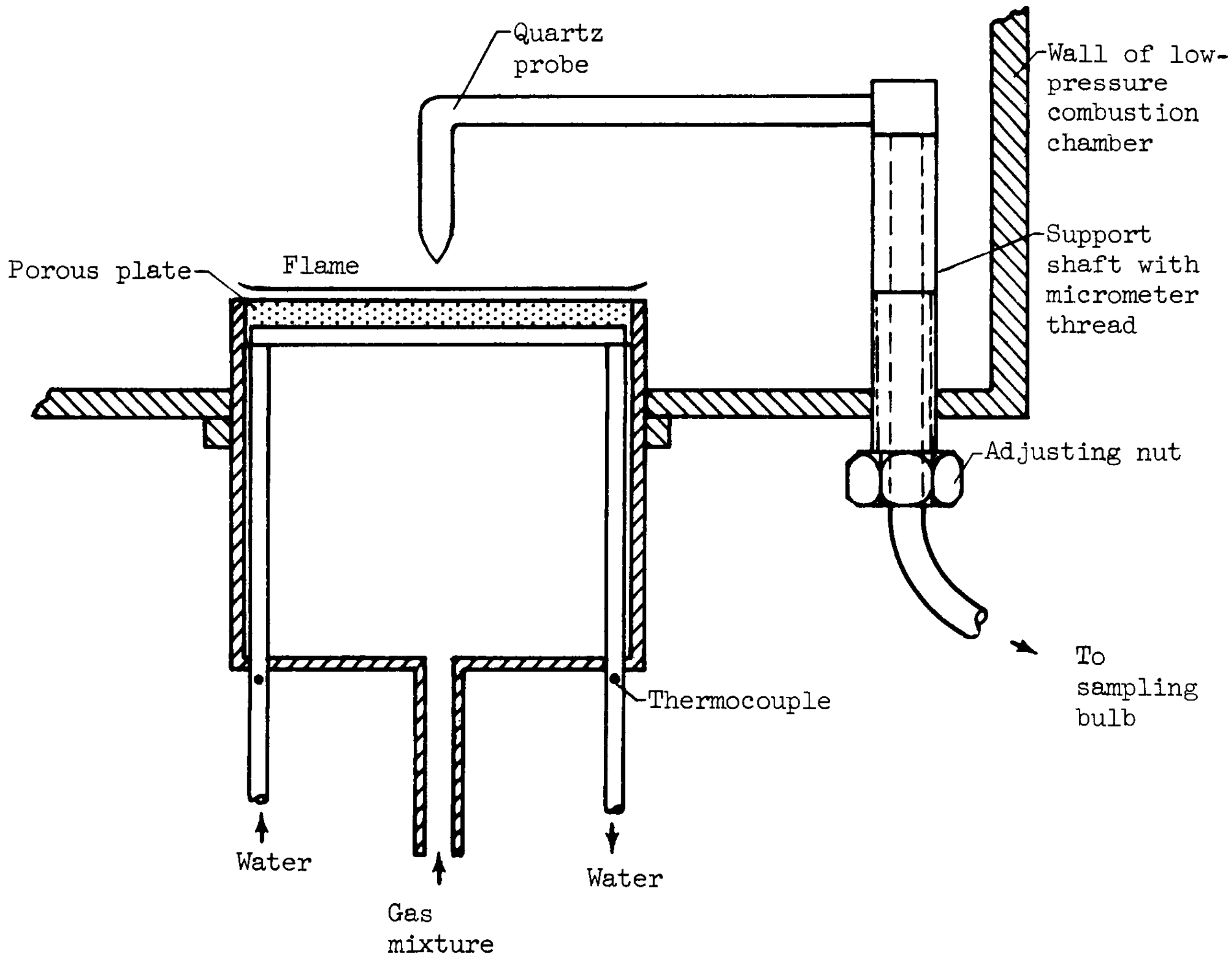

Figure 1. - Porous plate burner and sampling probe.

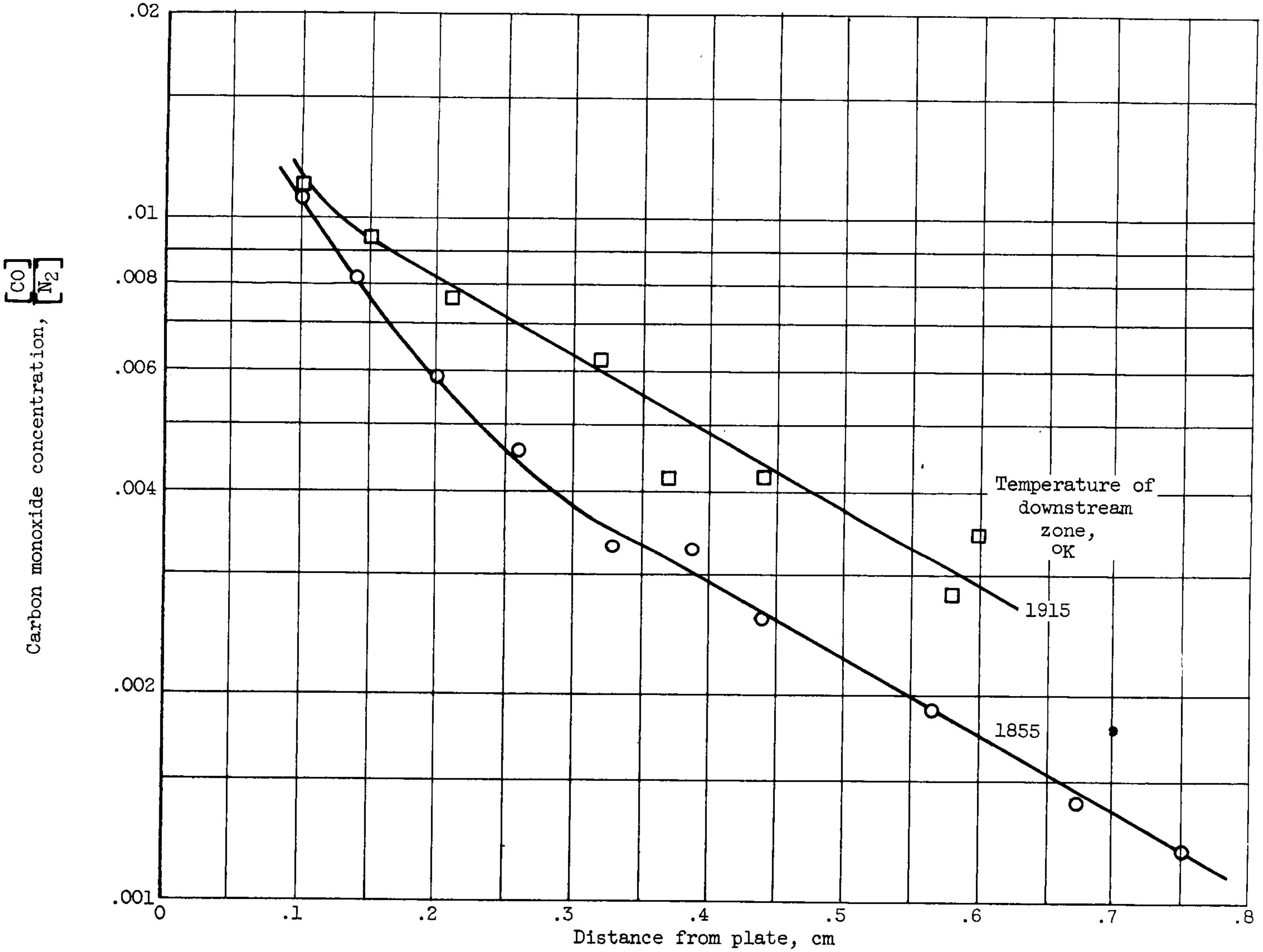

Figure 2. - Effect of temperature on carbon monoxide decay. Equivalence ratio, 0.835; pressure, 1 atmosphere; 2-inch burner.

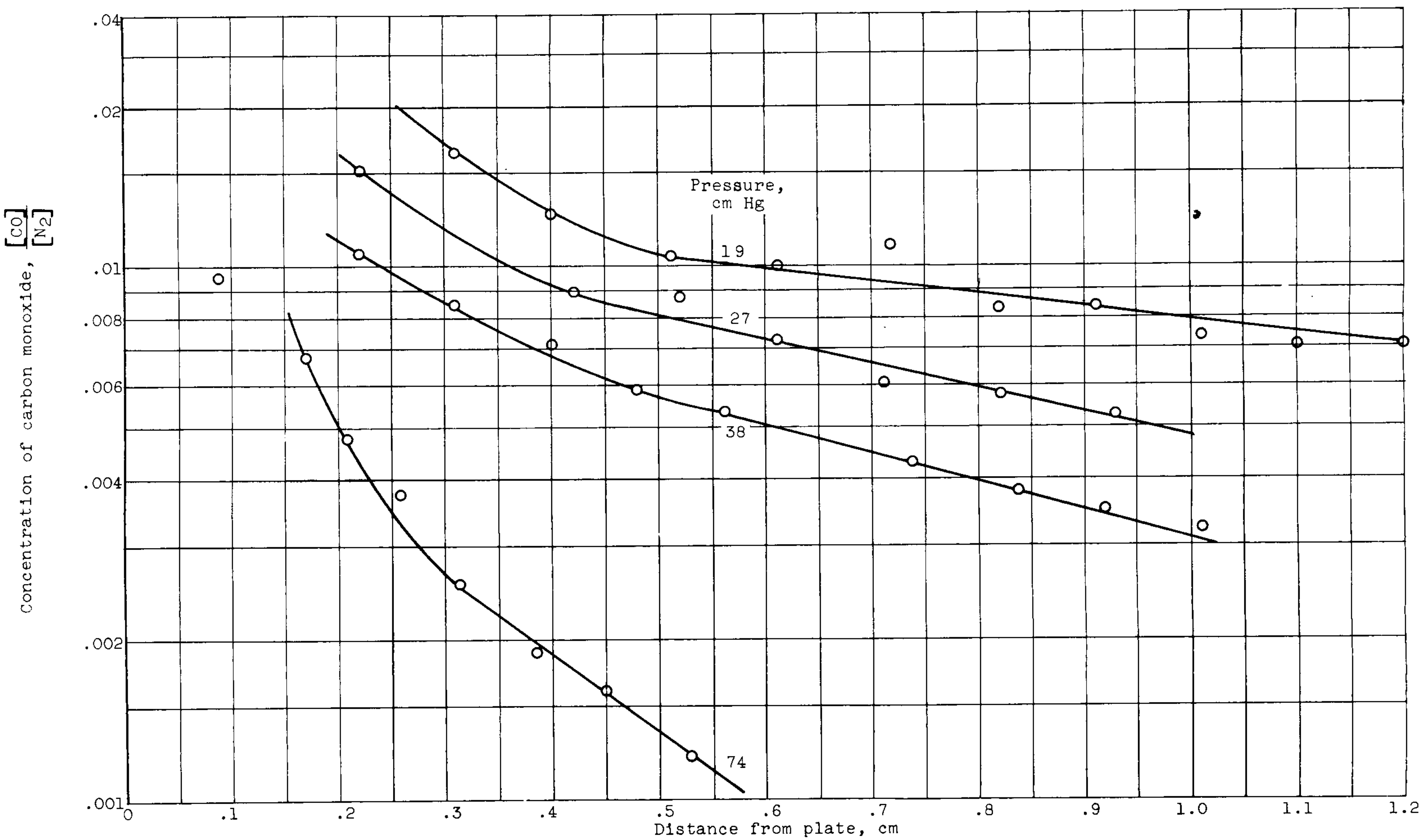

Figure 3. - Effect of pressure on carbon monoxide decay. Equivalence ratio, 0.86; temperature, 1870° K; 4-inch burner.

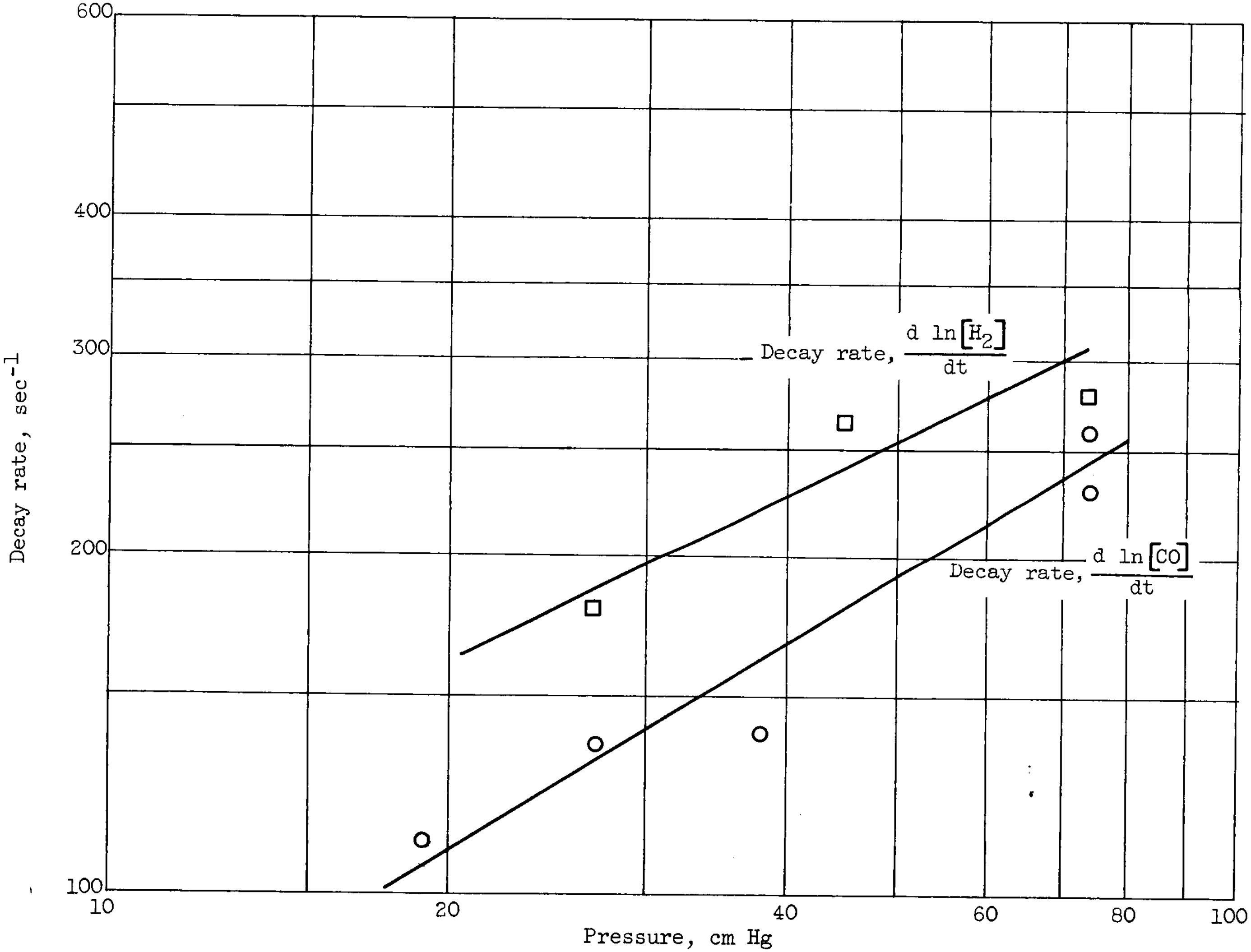

Figure 4. - Change of decay rates for carbon monoxide and hydrogen with pressure in propane-air flame. Four-inch burner.

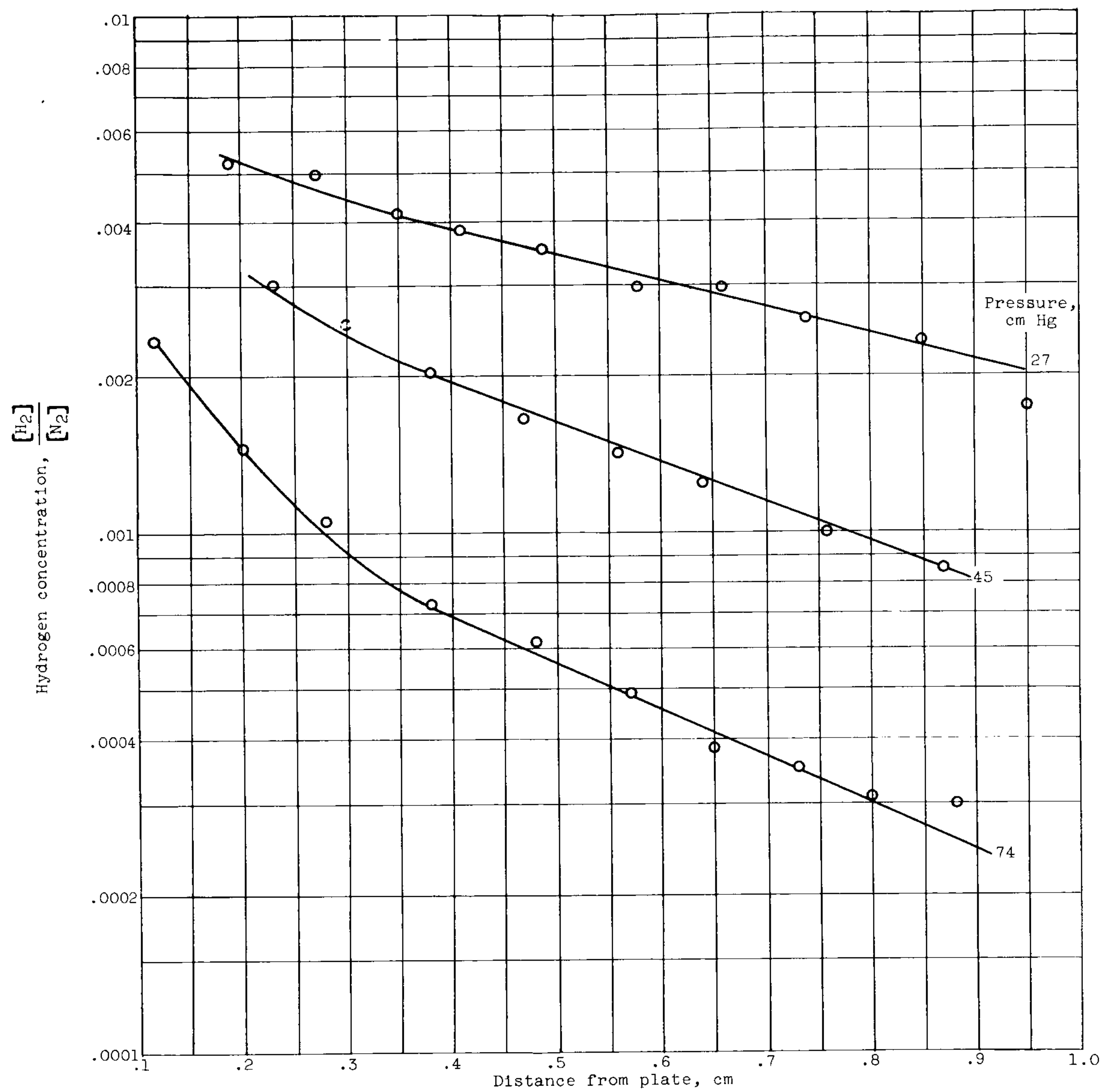

Figure 5. - Decay of hydrogen from propane-air flame. Equivalence ratio, 0.86; temperature, 1870° K; 4-inch burner.

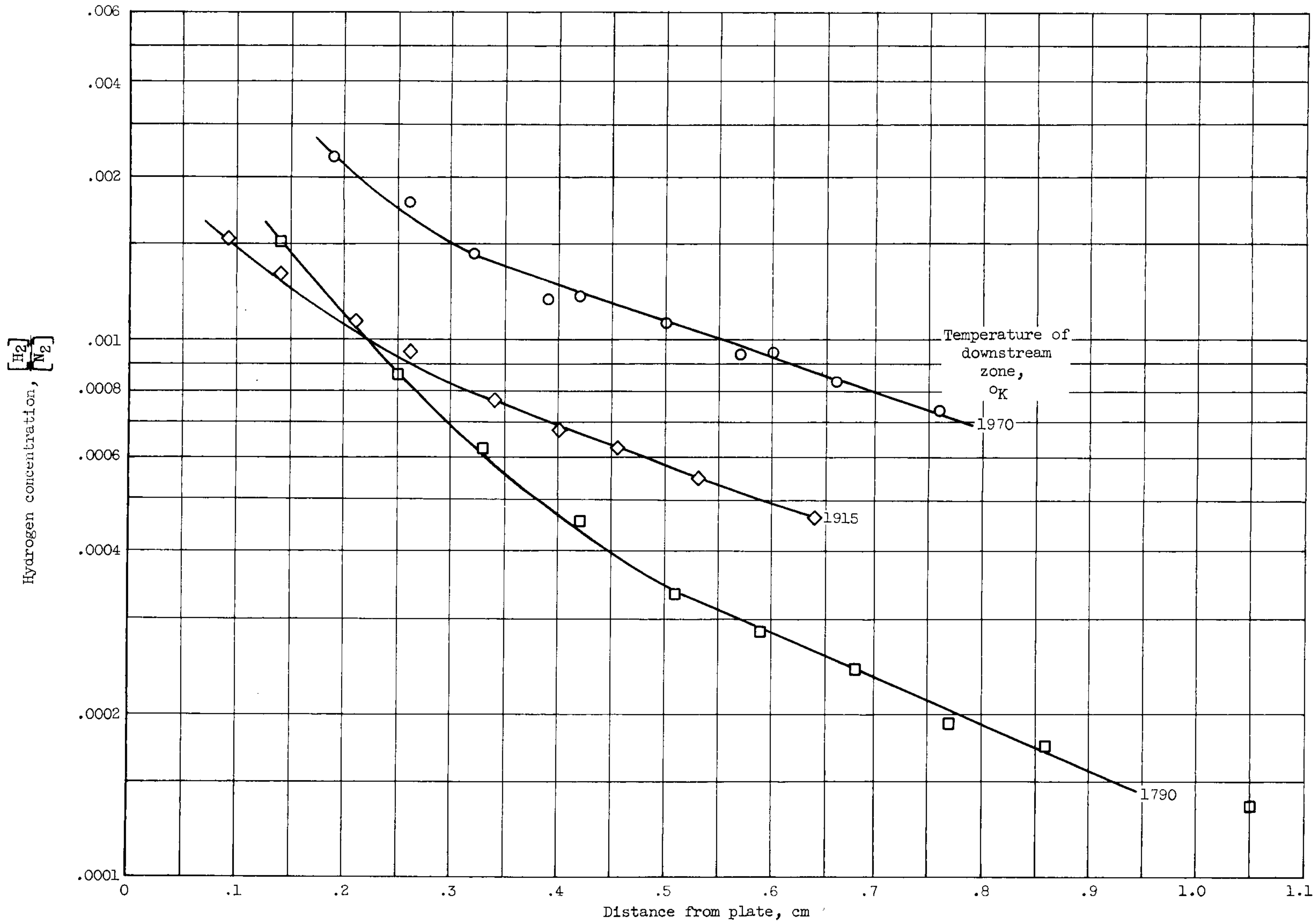

Figure 6. - Effect of temperature on hydrogen decay from propane-air flame. Equivalence ratio, 0.835; pressure, 1 atmosphere; 2-inch burner.

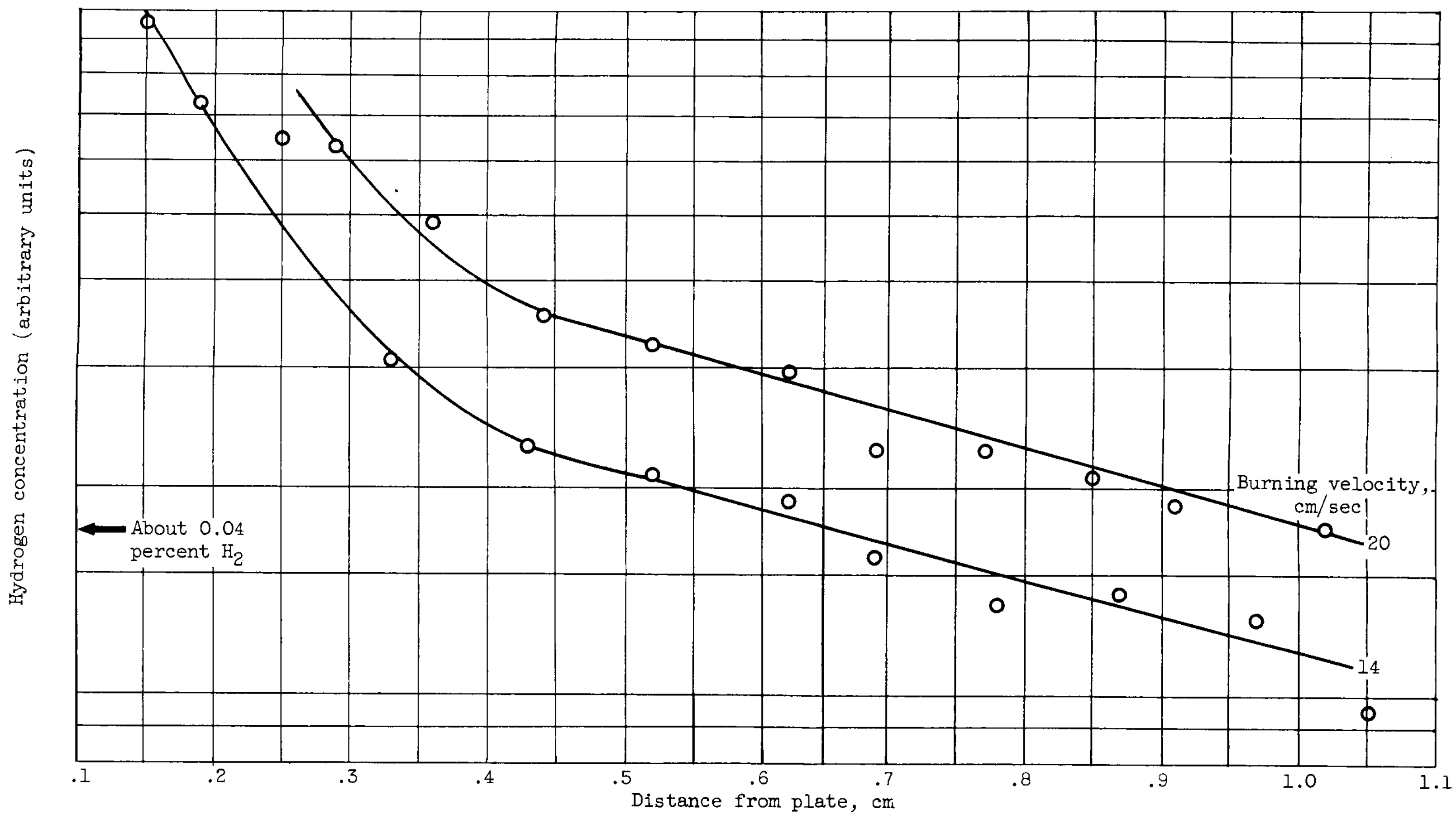

Figure 7. - Decay of hydrogen from propane-oxygen-argon flame. Pressure, 1 atmosphere; 2-inch burner.

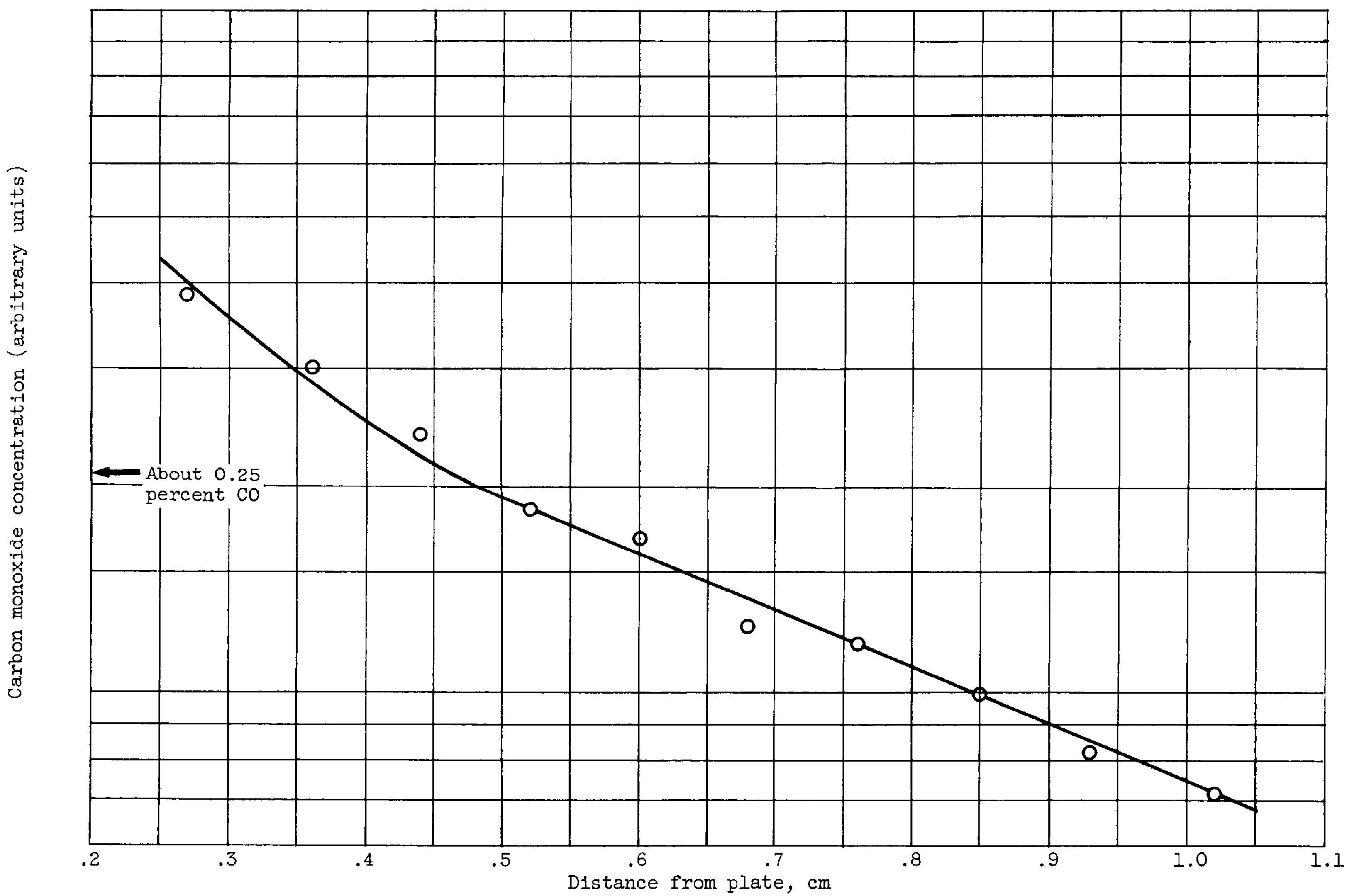

Figure 8. - Decay of carbon monoxide downstream of propane-oxygen-argon flame. Equivalence ratio, 0.835; pressure, 1 atmosphere; burning velocity, 14 centimeters per second; 2-inch burner.

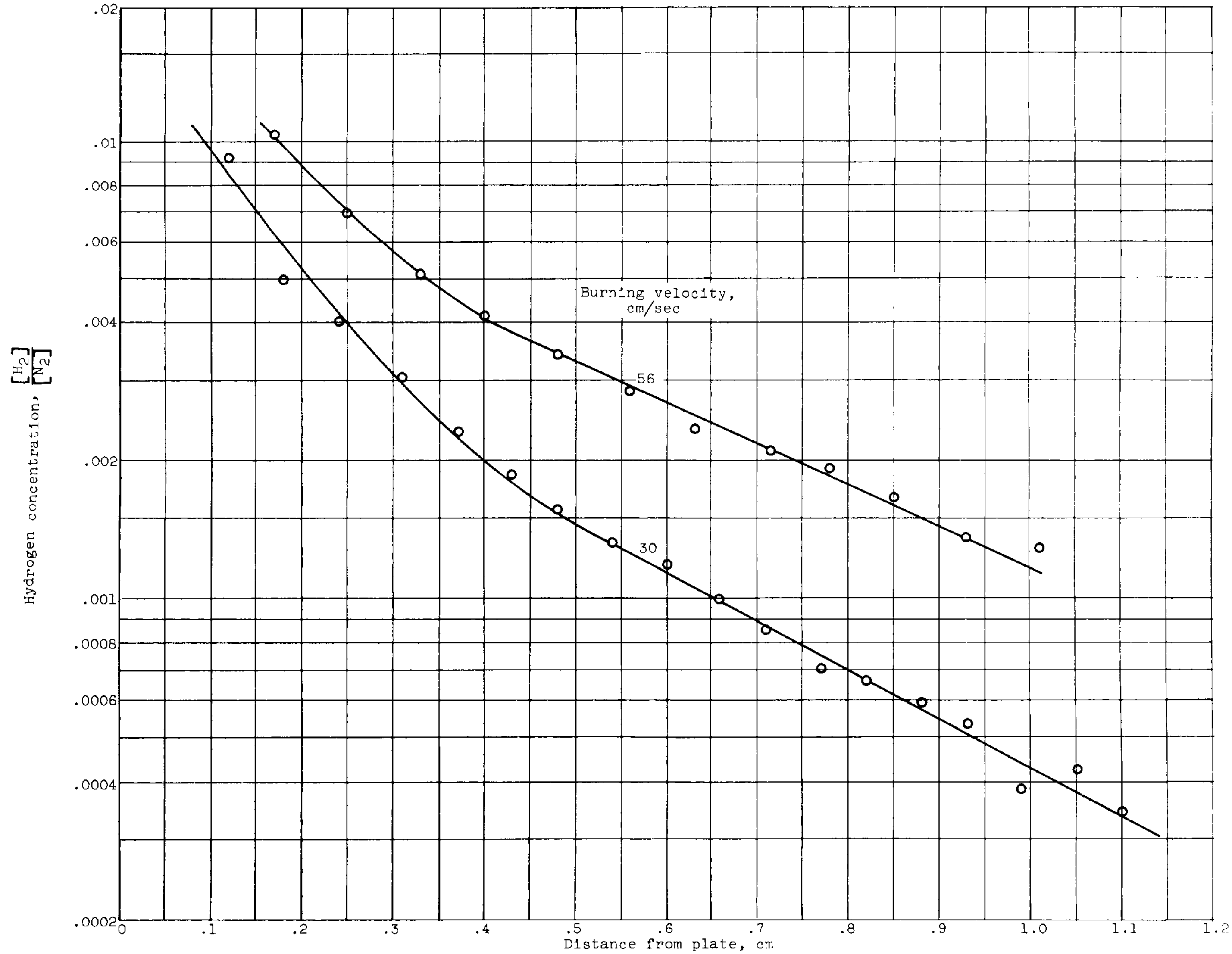

Figure 9. - Decay of hydrogen from hydrogen-air flame. Equivalence ratio, 0.70; pressure, 31 centimeters of mercury; 2-inch burner.

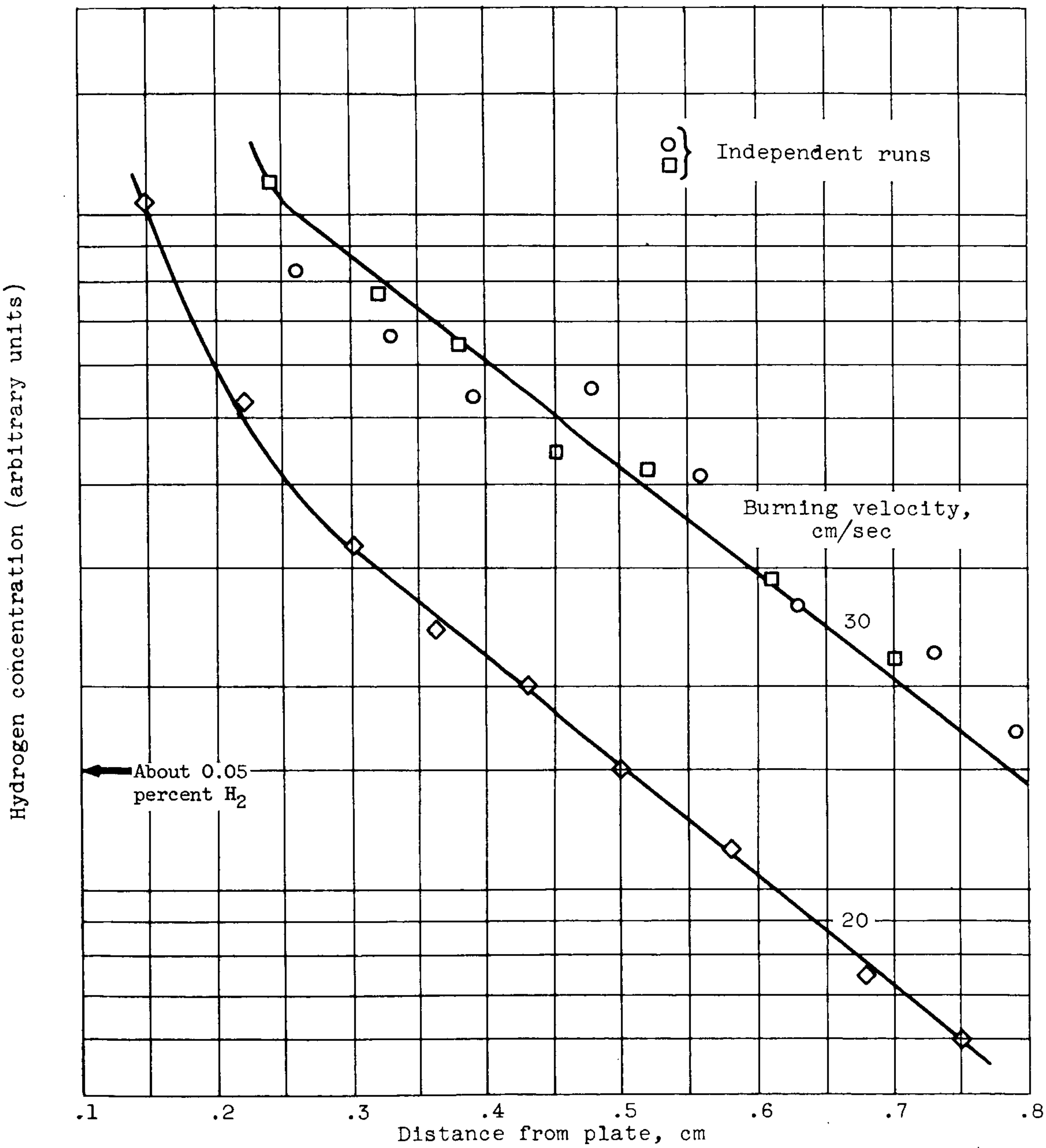

Figure 10. - Hydrogen decay downstream of hydrogen-oxygen-argon flame. Equivalence ratio, 0.600; pressure, 31 centimeters of mercury; 2-inch burner.